

PCT

WORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau



INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification 6 : C08F 10/00, 4/646		A1	(11) International Publication Number: WO 95/21203 (43) International Publication Date: 10 August 1995 (10.08.95)
(21) International Application Number: PCT/US95/01499 (22) International Filing Date: 6 February 1995 (06.02.95)		(81) Designated States: CA, CN, FI, JP, KR, MX, NO, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).	
(30) Priority Data: 08/192,217 4 February 1994 (04.02.94) US		Published <i>With international search report. Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i>	
(71) Applicant: EXXON CHEMICAL PATENTS INC. [US/US]; 5200 Bayway Drive, Baytown, TX 77520 (US).			
(72) Inventors: MIRO, Nemesio, Delgado; 2602 Cypress Court, Seabrook, TX 77586 (US). GEORGELLIS, George Byron; Apartment 683, 12903 Brant Rock, Houston, TX 77082 (US). SWEI, Homer, 7200 Almeda #502, Houston, TX 77054 (US).			
(74) Agents: MULCAHY, Robert, W.; Exxon Chemical Company, P.O. Box 2149, Baytown, TX 77522 (US) et al.			
(54) Title: DUAL DONOR CATALYST SYSTEM FOR THE POLYMERIZATION OF OLEFINS			
(57) Abstract			
<p>The present invention provides a catalyst system that exhibits unexpected control of desired properties in polyolefin products. The catalyst system includes a titanium-supported catalyst in combination with a mixture of tetraethoxysilane (TEOS) and dicyclopentyldimethoxy-silane (DCPMS). This catalyst system has been found to be effective in making polypropylene and polypropylene copolymers having relatively high melt flow rates and moderately broad molecular weight distribution.</p>			

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AT	Austria	GB	United Kingdom	MR	Mauritania
AU	Australia	GE	Georgia	MW	Malawi
BB	Barbados	GN	Guinea	NE	Niger
BE	Belgium	GR	Greece	NL	Netherlands
BF	Burkina Faso	HU	Hungary	NO	Norway
BG	Bulgaria	IE	Ireland	NZ	New Zealand
BJ	Benin	IT	Italy	PL	Poland
BR	Brazil	JP	Japan	PT	Portugal
BY	Belarus	KE	Kenya	RO	Romania
CA	Canada	KG	Kyrgyzstan	RU	Russian Federation
CF	Central African Republic	KP	Democratic People's Republic of Korea	SD	Sudan
CG	Congo	KR	Republic of Korea	SE	Sweden
CH	Switzerland	KZ	Kazakhstan	SI	Slovenia
CI	Côte d'Ivoire	LI	Liechtenstein	SK	Slovakia
CM	Cameroon	LK	Sri Lanka	SN	Senegal
CN	China	LU	Luxembourg	TD	Chad
CS	Czechoslovakia	LV	Latvia	TG	Togo
CZ	Czech Republic	MC	Monaco	TJ	Tajikistan
DE	Germany	MD	Republic of Moldova	TT	Trinidad and Tobago
DK	Denmark	MG	Madagascar	UA	Ukraine
ES	Spain	ML	Mali	US	United States of America
FI	Finland	MN	Mongolia	UZ	Uzbekistan
FR	France			VN	Viet Nam
GA	Gabon				

"Dual Donor Catalyst System For The Polymerization Of Olefins"

5

BACKGROUND

Field of the Invention

10 The present invention relates to catalyst components for olefin polymerization which can produce polyolefins, and in particular polypropylene having high crystallinity and relationship high melt flow rates (MFR), and consequently, suitable processing properties.

15 **Description of the prior art**

 The homopolymers and copolymers of propylene generally have certain properties that are unsatisfactory for specific applications. It therefore becomes necessary to modify certain characteristics during the manufacture of the polypropylene to render the polymer more useful for a 20 certain end results. For example, if the rigidity of the polymer or copolymer of propylene is improved, it is possible to reduce the thickness of the resulting molded product formed from it.

 There are numerous polymerization and copolymerization 25 processes and catalyst systems in the prior art from which it is possible to tailor a processing catalyst system to obtain a specific set of properties of a resulting polymer or copolymer. For example, in certain applications, a product with higher melt flow rate is desirable. Such a product has a lower melt viscosity than a product with a lower melt flow rate. Many polymer or 30 copolymer fabrication processes which operate with high shear rates, such

as injection molding, oriented film and thermobonded fibers, would benefit from a lower viscosity product by improving through-put rates and reducing energy costs. Generally, olefin polymers obtained by using an active catalyst component of the magnesium ($MgCl_2$) supported type have 5 a limited melt flow rate range and mechanical properties. As indicated, however, for certain applications, polypropylene polymers which flow readily during melting have improved processing characteristics.

A discovery of more appropriate co-catalysts or electron donors to 10 accompany supported magnesium catalyst components have been of great benefit to improving the efficiency of the catalyst system and the quality control of the polymer product. In such catalyst systems, the cocatalyst activates the catalyst and provides initiation of a polymer chain. The cocatalyst that has historically worked well with magnesium supported 15 catalysts is organo aluminum compounds, most typically triethylaluminum ("TEAL"), or other trialkyl aluminum compounds. Examples of other useful organoaluminum compounds include an alkylaluminum dihalide, a trialkoxyaluminum, a dialkylaluminum halide and a triisobutyl aluminum.

20 An electron donor compound is used in the polymerization reactor to control the stereoregularity and form of the polymer. Although a broad range of compounds are known generally as electron donors, a particular catalyst may have a specific compound or groups of compounds with which it is especially compatible. Discovery of an appropriate type of 25 electron donor can lead to significant improvement in the properties of the polymer product such as molecular weight distribution and melt flow. Discovery of a specific group of electron donors for magnesium supported

catalysts that would provide beneficial results would be highly advantageous.

The present invention is directed to the use of a mixture of silane electron donors. In Mitsui EP 385765A (published 9/5/90), there is demonstrated a catalyst system composed of a magnesium supported titanium catalyst component in combination with two silane electron donors, a specific donor mixture embodiment of which is directed to dicyclopentyl dimethoxysilane ("DCPMS") and propyltriethoxysilane ("PTES"). In U. S. Patent number 5,100,981, disclosed is a catalyst system composed of a magnesium supported titanium catalyst and a mixture of two electron donors, cyclohexylmethyl dimethoxysilane ("CMMS") and phenyltriethoxy silane ("PES").

It has now been surprisingly found that the use of two different organosilicon compounds as electron donors in combination with a magnesium supported catalyst is capable of generating highly isotactic polypropylene polymers having a moderately broad molecular weight distribution as well as relatively high melt flow rates.

20

Summary of the Invention

It has been found that a catalyst system based on a solid magnesium supported catalyst component, an organoaluminum co-catalyst component, and a mixture of two different electron donors, one of which functionally dominates the other, is capable of achieving highly crystalline polyolefins having the characteristics of moderately broad

molecular weight distribution and relatively high melt flow rates. In a preferred embodiment, two organosilicon compound electron donors, dicyclopentydimethoxysilane ("DCPMS") and tetraethoxysilane ("TEOS") have been found to provide an optimum electron donor mixture in the 5 instant catalyst system invention. It has been discovered that DCPMS acts as the dominant donor in combination with the weaker donor TEOS. It is found that a mixture of the two donors in a catalyst system generates isotactic polypropylene having product characteristics similar to the polypropylene product generated by a supported catalyst system 10 employing 100% DCPMS such as high crystallinity and low melt flow rate. This discovery enables the use of the weaker donor to make polyolefin polymers in a first stage reaction with the polymer characteristics of the TEOS donor, i.e. high MFR, and polymerizing the resulting polyolefin in a second stage reaction with a mixture of the weak donor ("TEOS") and the 15 stronger donor ("DCPMS") to achieve a final highly crystallinity polyolefin polymer having beneficial characteristics of relatively high MFR and moderately broad MWD, these polymer characteristics being otherwise independently obtainable by the sole use of each silane electron donor. In summary, the use of the present dual donor system enables the 20 production of a final polyolefin product with relatively high MFR, a moderately broad MWD similar to that of DCPMS generated polymers.

The surprising and unexpected result in the use of the dual donor system of the present invention lies in the dominant feature of the DCPMS. 25 Ordinarily, it would have been expected that the use of DCPMS in combination with TEOS would result in physical characteristics in the ultimate polymer attributable to the proportionate amount of each electron

donor used. However, the discovery that the use of these two donors in a catalyst system generates polyolefins with properties attributable to the dominant electron donor, DCPMS, has resulted in the development of a two stage polymerization process in which a high MFR polyolefin product 5 is made in the first stage through the use of the TEOS donor, while the second stage reaction utilizing a mixture of TEOS/DCPMS enables production of a highly crystalline polyolefin having the characteristics of moderately broad molecular weight distribution and relatively high MFR. In summary, the use of TEOS as an electron donor in a first stage olefin 10 polymerization reaction, followed by introduction of the electron donor DCPMS in a second stage reaction has resulted in the production of crystalline polyolefin products having the characteristics of moderately broad polymer MWDs and relatively high MFRs.

15 The present invention provides a catalyst system for the polymerization of olefins comprising:

- (A) a solid magnesium supported titanium catalyst component;
- 20 (B) an organoaluminum cocatalyst; and
- (C) a Dual Donor catalyst system comprising (1) a first electron donor compound, and (2) a second dominating electron donor compound, wherein, the MFR (a) of a polyolefin obtained by polymerizing an alpha-olefin in the presence of dominating electron donor (2) and, the MFR (b) of polyolefin 25 polymerized under the same polymerization conditions, but

using a mixed donor system of 50 mole percent (1) and 50 mole percent (2), satisfy the relationship.

$$5 \quad \text{LOG} \quad \left| \frac{[\text{MFR(a)}]}{[\text{MFR(b)}]} \right| \quad \text{is} \leq 1.2.$$

The present invention is further directed to a process for making a
10 homopolymer or copolymer, or a reactor blend of homopolymer and
copolymer (impact copolymer), of an alpha-olefin having a relatively high
melt flow rate, high crystallinity and moderately broad molecular weight
distribution comprising polymerizing an alpha-olefin in a multi-stage
reaction in the presence of (1) a high activity magnesium supported
15 titanium catalyst system, (2) an organoaluminum co-catalyst, and (3) an
electron donor mixture of two different compounds in at least two stages,
comprising:

(A) in the first stage, polymerizing the alpha-olefin in the
20 presence of a first electron donor (i) to produce a polyolefin,
and

(B) in another stage, further polymerizing the polyolefin polymer
of stage one in the presence of a donor mixture of the
25 electron donor (i) and a dominating electron donor (ii) to
achieve a final polyolefin.

Brief Description of the Drawings

Figure 1 is a graph demonstrating the relationship between MFR and absorption of hydrogen in the use of TEOS and DCPMS, respectively.

5 Figure 2 is a graph plotting the relationship between MFR of the present polyolefins in relation to varying quantities of the dual electron donors of the present invention.

10 Figure 3 is a graph plotting the relationship of the heater fusion of polyolefin prepared using varying quantities of the dual electron donors of the present invention.

15 Figure 4 is a graph plotting the relationship between the heat of fusion and the log of melt flow rates of polymer prepared in a single stage process, and comparing the heat of fusion with the multi-stage process of the present invention.

Detailed Description of Invention

The present invention is directed to the combination of a mixture of 20 two electron donors ("Dual Donors") with a particular type of catalyst component for use in the polymerization of polyolefins. This combination of Dual Donor and catalyst component comprises a catalyst system that results in better control of crystallinity and melt flow rate than that provided alone by either electron donor compound of the Dual Donor system.

25 Moreover, the instant catalyst system maintains a high catalyst efficiency relative to other suitable catalyst systems and, further, the catalyst system of the present invention retains most of its high activity over time. These

and other beneficial advantages will become more apparent from the following detailed description of the invention and the accompanying examples.

5 Electron donors are typically used in two ways in the formation of a Ziegler-Natta catalyst and a catalyst system. First, an internal electron donor may be used in the formation reaction of the catalyst as the transition metal halide is reacted with the metal hydride or metal alkyl. Examples of internal electron donors include: amines, amides, ethers, 10 esters, aromatic esters, ketones, nitriles, phosphines, stibines, arsines, phosphoramides, thioethers, thioesters, aldehydes, alcoholates, and salts of organic acids. The second use for an electron donor in a catalyst system is as an external electron donor and stereoregulator in the polymerization reaction. The same compound may be used in both 15 instances, although typically they are different. A common external electron donor is an organic silicon compound, for example, tetraethoxysilane, one of the Dual Donors used in the present invention. A description of the two types of electron donors is provided in U. S. Patent number 4,535,068, the disclosure of which is hereby incorporated by 20 reference.

As the present invention relates particularly to external electron donors, the term "electron donor" as used herein, refers to the external donor. The external electron donor acts as a stereoregulator to control the 25 amount of atactic form of polymer produced. It may also increase the production of isotactic polymers. In these functions, the MWD, high crystallinity, and MFR of produced polymer will be affected by the particular

donor used. Organic silicon compounds are known in the art for use as electron donors. Examples of electron donors that are organic silicon compounds are disclosed in U. S. Patent numbers 4,218,339; 4,395,360; 4,328,122; and 4,473,660. As mentioned, a particular catalyst may 5 produce better results when paired with a particular group of electron donors. Examples of this paring of catalyst and electron donors are disclosed in U. S. Patent numbers 4,562,173 and 4,547,552.

The effectiveness of the electron donor depends largely on its 10 compatibility with the catalyst with which it is used. Apparently, there is some electrical and/or steric compatibility between certain donors and particular catalysts that yields better results than with the same catalyst and less compatible donors. This compatibility is not totally understood, nor is it predictable as there are no outward suggestions that one electron 15 donor would work better than another with a particular catalyst, and as demonstrated by the present invention, it may be discovered that a certain combination of electron donors are more compatible with a particular type of catalyst than would have been predictable.

20 It has been discovered herein that a particular combination of electron donors does significantly enhance the catalytic properties of a specific type of catalyst. The catalyst involved in the present invention is a Ziegler-Natta type titanium catalyst for the polymerization of olefins. The instant catalyst system comprises a solid titanium catalyst component in 25 combination with a Dual Donor, and is comprised of:

- (A) a highly active magnesium supported titanium catalyst component consisting essentially of magnesium, titanium, halogen and an internal electron donor,
- 5 (B) an organoaluminum compound, and
- (C) a Dual Donor wherein one electron donor compound dominates the other.

10 The processes for polymerizing or copolymerizing olefins in the presence of these Ziegler-Natta type catalysts are disclosed in Japanese Laid-Open Patent Publications numbers 83006/1983, 138705/1983, 138706/1983, 138707/1983, 138708/1983, 138709/1983, 138710/10 and 138715/1983). Typical solid titanium supported catalyst systems and 15 preparations thereof are outlined in U. S. Patent numbers 4,990,479 and 5,159,021, the disclosures of which are hereby incorporated by reference.

20 Briefly, catalyst component (A) can be obtained by (i) suspending the dialkoxy magnesium in an aromatic hydrocarbon that is liquid at normal temperatures, (ii) contacting the dialkoxy magnesium with a titanium halide and further (iii) contacting the resulting composition a second time with the titanium halide, and contacting the dialkoxy magnesium with a diester of an aromatic dicarboxylic acid at some point during the treatment with the titanium halide in (ii).

25

Component B of the instant catalyst system is an organoaluminum co-catalyst. The organoaluminum compound should be halogen-free.

Suitable halogen-free organoaluminum compounds (component B) are, in particular, branched, unsubstituted alkylaluminum compounds of the formula AlR_3 , where R denotes an alkyl radical having 1 to 10 carbon atoms, such as for example, trimethylaluminum, triethylaluminum, 5 triisobutylaluminum, and tridiisobutylaluminum. Further suitable compounds are readily available and amply disclosed in the prior art including U. S. Patent number 4,990,477 hereby incorporated by reference.

10 The above-described magnesium supported catalysts component (A) exhibits comparable efficiency to previously known catalyst systems when the component (A) is paired with an appropriate silane electron donor, such as TEOS or DCPMS, but that control is significantly enhanced when the catalyst is paired with a combination of both these electron 15 donors when used in the multi-stage process of the present invention. This improved isotacticity/MFR control results in an enhanced control of the properties of the polymer product.

In a preferred embodiment of the present invention, the external 20 electron donors chosen are the silane compounds dicyclopentyl-dimethoxysilane and tetraethoxysilane. It has been found that when these silanes are used in combination as a Dual Donor in a magnesium supported catalyst system, the DCPMS acts as a dominant donor in generating polyolefins having crystallinity (heat of fusion) and MFR 25 properties similar to that resulting from the sole use of DCPMS. This discovery enables a two stage olefin polymerization process in which the weaker donor, TEOS, is used in the first stage to make polyolefins with the

higher MFR characteristics of TEOS and employed in a second stage, a mixture of TEOS and DCPMS polymerization to produce a final polyolefin with a relatively high MFR, high crystallinity, and moderately broad MWD.

5 While a combination of polymer characteristics might ordinarily be expected from the use of a catalyst system employing two different stereoregulating electron donors, the unexpected result here is that there is a dominant donor effect and that the effects of the two donors is not averaged. As a result, minor amounts of DCPMS can be used in

10 combination with TEOS to generate polyolefin polymers having the high crystallinity, and low MFR associated with the use of DCPMS. Operable amounts of the DCPMS silane electron donor of the preferred Dual Donor mixture are from about 10-99 mole percent DCPMS, the TEOS being present in quantities of from about 90-1 mole percent. A preferred ratio of

15 DCPMS to TEOS is from about 30-70% DCPMS and from 70-30% TEOS. Most preferred ratios of DCPMS to TEOS, in the Dual Donor catalyst system of the present invention are 45-55 mol percent DCPMS to 55-45 mole percent TEOS.

20 Examples of olefins that can be used in the polymerization process of the present invention are alpha-olefins having 2 to 20 carbon atoms such as ethylene, propylene, 1-butene, 4-methyl-1-pentene, 1-octene, 1-hexene, 3-methyl-1-pentene, 3-methyl-1-butene, 1-decene, 1-tetradecene, and 1-eicosene.

25

In another preferred embodiment of the invention, a multi-stage process for the preparation of a polyolefin is provided in which the alpha-

olefin is polymerized in two stages in the presence of (1) a magnesium supported catalyst system, and (2) an electron donor mixture of the two silane compounds, TEOS and DCPMS, comprising the steps of:

- 5 (A) a first stage polymerizing alpha-olefin in the presence of TEOS silane electron donor to produce a polyolefin having an MFR of between 10 and 1200;
- 10 (B) in another stage, further polymerizing the polyolefin of step (A) in the presence of a mixture of TEOS/DCPMS thereby producing a polyolefin polymer having an MFR of between 1 and 120, and a MWD of less than 6.

15 The complete set of data for Figures 1, 2, and 3 are tabulated in Tables 1, 2, and 3. The MFR-H₂ response curves when using TEOS or DCPMS, respectively, are shown in Figure 1. It shows the very high MFRs typical of the TEOS donor; and low MFRs typical of the DCPMS donor. The complete set of data used to construct this figure are tabulated in Tables 1 and 2.

20 The dramatic dominance of DCPMS is demonstrated in Figures 2 and 3, showing the MFR and (ΔH) behavior as a function of the DCPMS/TEOS mole ratio polymerized in a batch reactor. Figure 2 shows that the MFR is virtually unchanged from 100% DCPMS to 10% DCPMS. 25 Figure 3 shows a similar behavior with crystallinity as measured by the DSC heat of melting. Again, the crystallinity is virtually unchanged from 100 to 10% DCPMS.

TABLE I
EFFECT OF HYDROGEN ON MFR WITH TEOS AS REACTOR DONOR

Catalyst	Run No. 11373	Cat (mgs)	TEOS (mmole)	Polymerization Conditions			Polymerization Results			DSC Results		
				DCPMS (mmole)	Hydrogen (psi, 300°C)	Activity (Kg/g η)	MFR (dg/min)	HI (%)	T _c °C	ΔH _c J/g	T _m °C	ΔH _m J/g
TOHO- THC-C	135-026	7.25	0.2	-	10	5.1	3.09	-	110.5	103.3	158.9	102.6
	135-029	7.23	0.2	-	40	20.0	26.4	-	109.5	109.8	158.4	109.4
	120-019	5.44	0.2	-	40	16.7	31.2	96.0	-	-	-	-
	122-032	15.8	0.2	-	80	20.7	53.2	94.9	-	-	-	-
	126-034	15.4	0.2	-	80	12.4	89.2	95.0	-	-	-	-
	127-002	13.5	0.2	-	150	13.2	197.0	95.4	-	-	-	-
	135-032	7.23	0.2	-	150		229.9	94.4	-	-	-	-
Mitsui	126-022	15.0	0.2	-	80	10.4	143.2	92.6	-	-	-	-
TK220	131-011	61.1	0.2	-	60	12.2	42.5	93.7	-	-	-	-

TABLE II
EFFECT OF HYDROGEN ON MFR WITH DCPMS AS REACTOR DONOR

Catalyst	Run No	Cat (mgs)	Polymerization Conditions			Polymerization Results			DSC Results			
			TEOS (mmole)	DCPMS (mmole)	Hydrogen (psi, 300cc)	Activity (Kg/9 h)	MFR (dg/min)	H (%)	T _c °C	ΔH _c J/g	T _m °C	ΔH _m J/g
TOHO-THC-C	135-022	6.9	-	0.2	40	17.4	5.68	97.1	114.7	117.0	163.2	115.6
	119-001	11.5	-	0.2	80	48.6	1.84	98.2	-	-	-	-
	120-018	6.24	-	0.2	80	20.9	1.76	98.4	-	-	-	-
	125-022	10.5	-	0.2	80	41.2	1.65	98.9	-	-	-	-
	125-021	9.0	-	0.2	80	42.1	1.26	98.9	-	-	-	-
	128-028	10.1	-	0.2	80	27.9	1.92	98.9	-	-	-	-
	135-024	8.0	-	0.2	150	64.3	4.07	98.0	-	-	-	-
	135-027	8.0	-	0.2	170	70.3	4.12	97.2	-	-	-	-
	133-020	13.6	-	0.2	400	31.7	16.8	-	-	-	-	-
Mitsui TK220	131-012	31.7	-	0.2	80	30.4	2.58	98.5	-	-	-	-

TABLE III
EFFECT OF HYDROGEN ON MFR WITH BOTH TEOS AND DCPMS AS REACTOR DONORS

Catalyst	Run No.	Cat. (mgs)	TEOS (mmole)	Polymerization Conditions			Polymerization Results			DSC Results		
				DCPMS (mmole)	Hydrogen (ps, 300cc)	Activity (Kg/g hr)	MFR (g/min)	HI (%)	T _c °C	ΔH _c J/g	T _m °C	ΔH _m J/g
TOHO- THC-C	136-017	11.7	0.010	0.190	150	38.2	10.02	97.1	112.0	108.0	162.2	107.8
	135-036	7.61	0.020	0.180	150	67.7	4.39	97.4	112.8	113.3	163.8	113.0
	129-014	15.6	0.032	0.168	150	16.5	2.37	97.1	-	-	-	-
	129-013	13.8	0.050	0.150	150	28.7	4.49	97.4	-	-	-	-
	135-037	7.86	0.060	0.140	150	59.9	8.72	97.0	115.4	117.1	164.6	114.3
	136-005	7.50	0.100	0.100	150	62.9	6.41	96.6	112.5	113.3	165.0	113.3
	128-020	15.9	0.100	0.100	150	36.4	4.46	98.1	-	-	-	-
	128-026	10.7	0.100	0.100	150	41.4	4.36	98.3	-	-	-	-
	130-007	12.0	0.100	0.100	150	23.0	2.06	98.5	-	-	-	-
	128-021	16.8	0.100	0.100	80	26.8	1.87	98.4	-	-	-	-
	128-027	11.8	0.100	0.100	80	39.1	2.68	98.4	-	-	-	-
	136-012	6.75	0.150	0.050	150	63.2	2.57	98.2	114.0	115.2	164.2	115.0
Mitsui TK220	131-035	18.5	0.100	0.100	80	17.2	3.57	97.8	-	-	-	-

TABLE IV

TWO-STAGE POLYMERIZATION USING DUAL DONOR

(A) First stage - one hour polymerization time

(B) Second stage - one hour polymerization time

COMPARATIVE EXAMPLE

TABLE V

HIGH MFR POLYPROPYLENE FROM USING TEOS ONLY

Catalyst	Run No. (137-3- Solid)	Polymerization Conditions				Polymerization Results				DSC Results			
		TEOS (mL/g)	DCPMS (mL/g)	Hydrogen psi (300cc)	Activity (kg/g·hr)	MER (dg/min)	T _c °C	ΔHC J/g	T _m °C	ΔH _m J/g			
Mitsui TK 220	131-011	61.1	0.2	-	60	12.2	42.5	93.7	109.0	94.8	158.1	97.2	

TABLE VI

DONOR	MWD
DCPMS	5.0
TEOS	6.1
DCPMS/TEOS (50/50)	5.2

5 Tables IV and V demonstrate the results using the two stage polymerization process of the present invention. It demonstrates higher crystallinity for the two stage polymer product compared to the use of TEOS alone, both are at the same MFR.

10 As additional evidence of the dominance of DCPMS over TEOS, Table VI above shows typical MWD obtained with polymerization using TEOS, DCPMS, and a 50/50 blend of TEOS/DCPMS, respectively. The MWD data of the mixed donor system is unexpected and atypical. Catalyst systems with two donors without a dominating donor, when mixed, should 15 produce polymers with a broader MWD than either polymer produced with a single donor. However, as can be appreciated from Table VI, the MWD of the mixed donor is not broader, and is very close to that of DCPMS.

20 Processes for practice of the instant mixed donor invention are outlined as follows:

A. Process for Polypropylene homopolymer/Impact copolymer polymerization in batch reactors

The polymerization of propylene within an autoclave batch reactor

5 using a mixed donor catalyst system shows the dominant nature of DCPMS over TEOS. In combination with a $TiCl_4$ magnesium supported catalyst system, donors generally stereoregulate the polymerization of propylene to make higher or lower crystallinity polymers and the split between the amount of isotactic, syndiotactic, and atactic polymer

10 produced as for the contribution of each of the mixed donors. DCPMS acts as a high stereoregulator donor, while TEOS is a low stereoregular donor. However, at the same H₂ level, DCPMS produces a much lower melt flow rate polymer than that of TEOS. When combined, the properties of the polymer produced follow much closer that of DCPMS than weighted

15 property averages of the two pure systems.

The batch polymerization of propylene based polymers using the mixed donor technology is used in two ways: (1) in a pure batch mode where the two donors are premixed and reacted with the magnesium supported $TiCl_4$ catalyst, made to form a slurry and injected into an autoclave type reactor, or (2) in a semi-batch mode composed of two stages. In the first stage only a single donor, TEOS, is premixed and reacted with the magnesium supported $TiCl_4$ catalyst, made into a slurry and injected into an autoclave type reactor. Polymerization with this single

20 donor catalyst system continues for some preset time period, followed by the injection of the second donor, DCPMS, where the polymerization again continues for a second preset time period. In the pure batch mode, the

25

polymer created closely resembles that of DCPMS alone; while in the semi-batch mode, only the polymer produced in the second stage closely resembles that of DCPMS. The semi-batch produced polymer therefore is effectively an intimate mixture of (A) high melt flow rate, low crystallinity
5 TEOS produced molecules and (B) low melt flow rate, high crystallinity TEOS/DCPMS produced molecules. The overall melt flow rate polymerization window of the semi-batch process however, is much greater than that of the pure batch process.

10 B. Continuous process for making impact copolymer

Polymerization was carried out using a multi-stage continuous process, where the first two reactors are of bulk liquid propylene slurry stirred tank reactors type, followed by an additional reactor of gas phase
15 fluidized bed reactor type. Polypropylene homopolymer is produced by a polymerization of propylene within the two Bulk Propylene Slurry reactors followed by a polymerization of 20-80% ethylene and 80-20% propylene copolymer within the Gas Phase reactor. This intimate mixture of homopolymer and ethylene/propylene copolymer is known in the trade as
20 an "Impact Copolymer (ICP)". The composition of the final product is an ICP having between 0-50% ethylene/propylene copolymer and 100-50% propylene homopolymer. The total percent ethylene of these products range from 0 to 25%; and typical ICP melt flow rates range from 0.1 to 200.

25 To achieve high MFR and moderately broad MWD products, the two silane donors, TEOS and DCPMS, are added separately to the two Bulk Liquid reactors: TEOS is first injected in the first reactor, followed by

DCPMS injection in the second reactor. In the configuration used, a recycle system is returned to the second reactor. (No additional donor is introduced during the ethylene/propylene polymerization step). This effectively creates a multi-stage process where the first reactor has

5 exclusively the TEOS donor, while the second reactor has a combination of TEOS and DCPMS. Since DCPMS is dominant over TEOS, the second mixed donor reactor behaves very closely to one with DCPMS by itself. A high MFR, high heat of fusion polymer is achieved. Alternatively if a high crystallinity ICP is desired, a recycle stream is returned to the first reactor.

10 In the instant description, a multi-stage process is created with TEOS and DCPMS within both reactors.

The following Examples and Comparative Examples illustrate the present invention and its various advantages in more detail. The results

15 are summarized in Tables 1-4.

Catalyst

The catalysts provided herein are magnesium supported catalysts sold commercially by Toho Titanium Corporation of Japan and identified as

20 THC-C type catalyst and that sold by Mitsui Petrochemical Corporation of Japan described as TK-220.

Example 1

(I) One stage polymerization

25

In a 2 liter autoclave polymerization reactor that has been cleaned, dried, and purged well with nitrogen was charged by a syringe the

millimoles of silane donor (0.1M solution in hexane), followed by the addition of 2 millimoles of TEAL (triethyl aluminum in hexane). After isolating the reactor, the required amount of hydrogen was introduced into the reactor as measured by the psi drop from a 300 cc vessel. The 1000 5 ml of propylene was next added into the reactor. This was followed by introducing the required amount of catalyst slurred in the mineral oil as 15 or 20 weight percent solids which was pushed into the reactor with 250 cc of propylene. The reactor contents temperature was raised from room temperature to 70°C, and the reaction was continued for 1 hour. After the 10 polymerization period, the excess propylene was vented out of the reactor and the polymer collected and dried in a vacuum oven. The polymer was pelletized with the addition of 500 ppm BHT, and samples were taken for heptane insoluble, MFR, MWD, and DSC measurements.

15 **Example 2**

(II) Two stage polymerization example

The polymerization process was similar to that of Example 1, except that initially 0.2 mmole of TEOS was introduced into the reactor and 750 ml 20 of propylene was first added into the reactor. After one hour polymerization, 0.2 mmol DCPMS was pushed into the reactor with 250 ml propylene, and the polymerization was continued for an additional one hour. The results showed 44.7 dg/min MFR, 94.0 HI, 12,600 gPP/g-cat-hr activity, and 4.72 polymer MWD. Analysis of the polymer showed the 25 following composition:

	First Stage	Second Stage	Final Product
Donor	TEOS	TEOS/DCPMS	
Activity (Kg/g hr)	10.0*	2.7***	
MFR	70.0*	7.0**	44.7
MWD	6.09*		4.72

* Obtained from Example 1

5 **Obtained from back calculation using log/log blending of MFRs from First and Second stage polymer amount and MFR

***Obtained by difference.

10 These results show that the back-calculated MFR from the second stage polymerization corresponds to the expected MFR from the Example 1 polymerization using a 50/50 mole blend of DCPMS/TEOS.

15 The following example is of a continuous two stage polymerization using the Dual Donor invention for making ICP.

Example 3

Two stage process

20 The continuous process consists of two bulk liquid reactors in series followed by a single gas phase reactor. Generally, homopolypropylene is polymerized within the bulk liquid reactors followed by an ethylene/propylene copolymerization. The final product is called an "impact copolymer ("ICP"). The Dual Donor two stage process consists of 25 feeding two different donors within the two liquid bulk reactors. In this example, TEOS is added in the first liquid reactor; and DCPMS is added in the second liquid reactor. In the lead reactor, the TEOS donor produces a

high MFR resin (20-1000), while in the tail reactor, the mixture of donors TEOS/DCPMS produces a lower MFR resin (0.1-100). The resultant polymer is transferred in to a gas phase reactor where an ethylene/propylene rubber is polymerized.

5

Typical process conditions used are given as follows.

Temperatures within the bulk liquid reactors range from 148 to 158°F. Hydrogen and triethylaluminum (TEAL) concentrations within the liquid reactors are 10,000 ppm and 60-78 ppm, respectively. TEOS 10 concentration within the first stage was 16 ppm, while within the second stage, a mixture of TEOS (15 ppm) and DCPMS (22 ppm) was used. Typical production splits between the first and second stage reactors are 65:35. Within the gas phase reactor, the temperature was 158°F at 200 psig, with an ethylene to monomers ratio of .305. The total amount of 15 ethylene/propylene copolymer produced within the gas phase reactor was 30% of the final ICP.

Comparative Examples

Two comparative examples of the Dual Donor system are given 20 using a single stage continuous process. This first comparative example employs the use of a mixture of TEOS and DCPMS polymerized under comparable conditions as that shown in the two stage process. The second comparative example employs the use of a single donor TEOS used under similar conditions as the two stage process.

Results

Figure 4 shows that the two stage/mixed donor process polymer has a higher balance of crystallinity vs. melt flow rate. The two stage process polymer has a high crystallinity (DSC crystallization temperature) and a high melt flow rate. This balance of crystallinity vs. melt flow rate produced by the two stage process is higher than is expected from the averaged properties of the two single stage processes (TEOS and TEOS/DCPMS). This data show a polymer synergy when polymerized in a two stage process.

10

The preferred embodiments of the present invention, as described above, are not intended to limit the scope of the present invention, as demonstrated by the claims which follow, since one skilled in the art can, with minimal experimentation, extend the scope of the embodiments.

We claim:

1. A catalyst system for the polymerization of olefins comprising:

5 (A) a solid magnesium supported titanium catalyst component;

(B) an organoaluminum co-catalyst; and

10 (C) a Dual Donor catalyst system comprising (1) a first electron donor compound, and (2) a second dominating electron donor compound, wherein the MFR (a) of a polyolefin obtained by polymerizing an alpha-olefin in the presence of dominating electron donor (2) and, the MFR (b) of polyolefin polymerized under the same polymerization conditions, but

15 using a mixed donor system of 50 mole percent (1) and 50 mole percent (2), satisfy the relationship:

$$\text{LOG} \left| \frac{[\text{MFR}(a)]}{[\text{MFR}(b)]} \right| \text{ is } \leq 1.2.$$

20 2. The catalyst system of claim 1 wherein both electron donors are silane compounds.

25 3. The catalyst system of claim 2 wherein the dominant silane electron donor is DCPMS.

4. The catalyst system of claim 3 wherein the other silane electron donor is TEOS.
5. The catalyst system of claim 4 wherein mole ratio of DCPMS/TEOS are from the ranges of from about 30-70 mole percent DCPMS and 70-30 mole percent TEOS.
6. The catalyst system of claim 5 wherein the mole ratio of DCPMS to TEOS are from the ranges of from about 45-55 mole percent DCPMS to 55-45 mole percent TEOS.
7. The catalyst system of claim 1 wherein the solid catalyst is a magnesium supported $TiCl_4$ catalyst comprises $TiCl_4$ and the organoaluminum co-catalyst is triethylaluminum.
8. A process for making a homopolymer or copolymer of an alpha-olefin comprising polymerizing an alpha-olefin in a multi-stage reaction in the presence of (1) a high activity magnesium supported titanium catalyst system, (2) an organoaluminum co-catalyst, and (3) an electron donor mixture of two different compounds in at least two stages, comprising:
 - (A) in the first stage, polymerizing the alpha-olefin in the presence of a first electron donor (i) to produce a polyolefin, and

5 (B) in another stage, further polymerizing the polyolefin polymer of stage one in the presence of a donor mixture of the electron donor (i) and a dominant electron donor (ii) to achieve a final polyolefin having a relatively high melt flow rate, high crystallinity, and moderately broad molecular weight distribution.

9. A method for making a homopolymer or copolymer of an alpha-olefin having relatively high crystallinity, melt flow rate and a moderately broad molecular weight distribution comprising polymerizing an alpha-olefin in the presence of (1) a high activity magnesium supported titanium catalyst system, (2) an organoaluminum co-catalyst, and (3) an electron donor mixture comprised of two different silane compounds in at least two stages, 10 comprising:

15 (A) in the first stage, polymerizing an alpha-olefin in the presence of TEOS to produce a polyolefin having an MFR of at least 10; and

20 (B) in another stage, further polymerizing the polyolefin polymer of stage one in the presence of the dominant donor DCPMS to achieve a polyolefin having an MFR of 0.1.

25 10. The method of claim 9 wherein the homopolymer or copolymer products formed in step (A) comprise at least 15 weight percent of the total amount of final homopolymer of polyolefin produced.

11. The method of claim 9 wherein the polymerization in each stage is performed continuously in series reactors.
- 5 12. The method of claim 11 wherein the polymerization performed in each stage is performed in the gas phase.
13. The method of claim 9 wherein the polymerization is performed in a single batch reactor.
- 10 14. The method of claim 9 wherein the ethylene weight ratio to propylene is present in the ratio of 20/80 mole percent.
- 15 15. The method of claim 9 wherein the mole percent ratio of the TEOS/DCPMS Dual Donor in stages (A) and (B) ranges from 10 to 90, to 95 to 5.
16. The method of claim 15 wherein the mole percent of the Dual Donor is 50 mole percent of each donor.

1/4

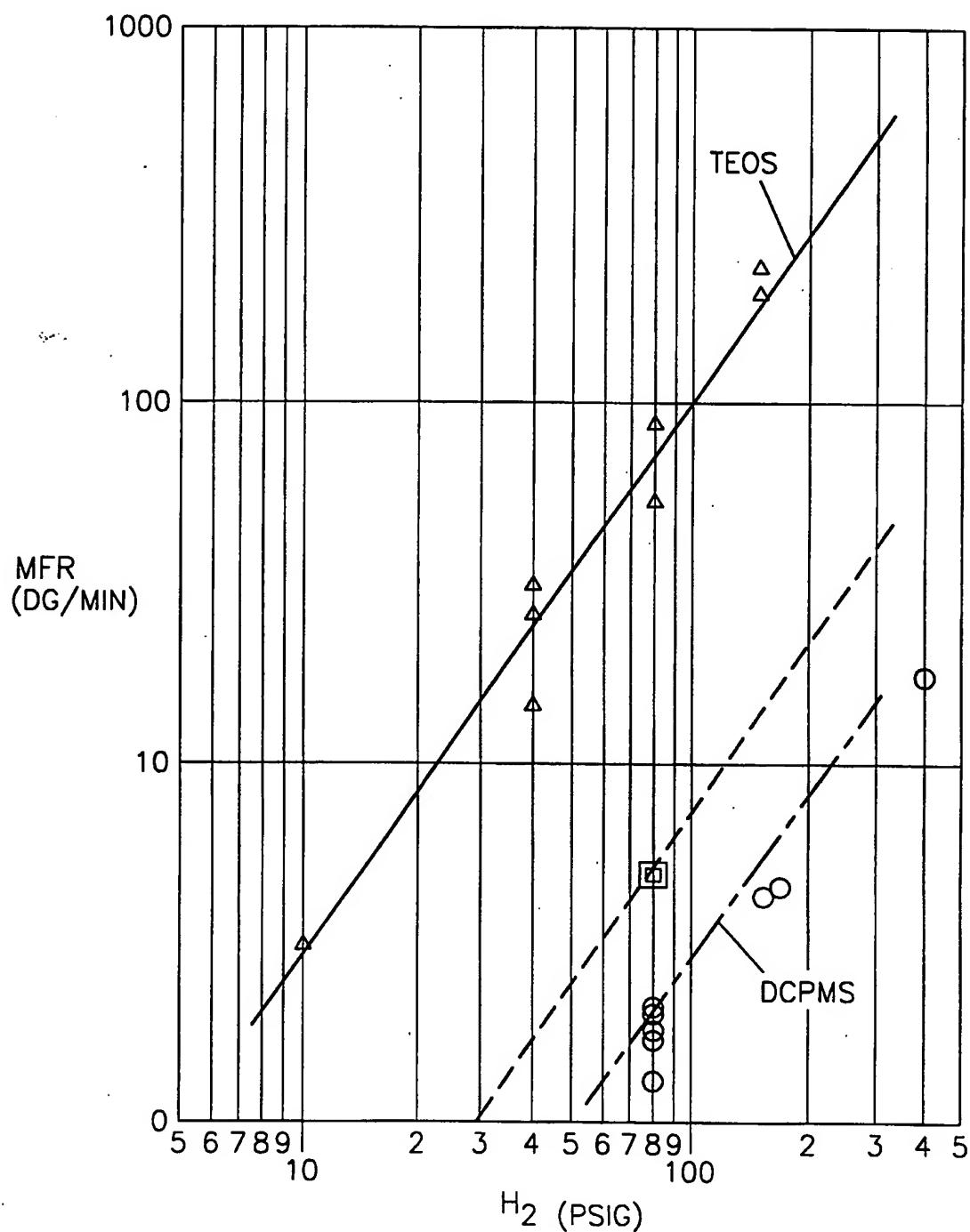


FIG. 1
SUBSTITUTE SHEET (RULE 26)

2/4

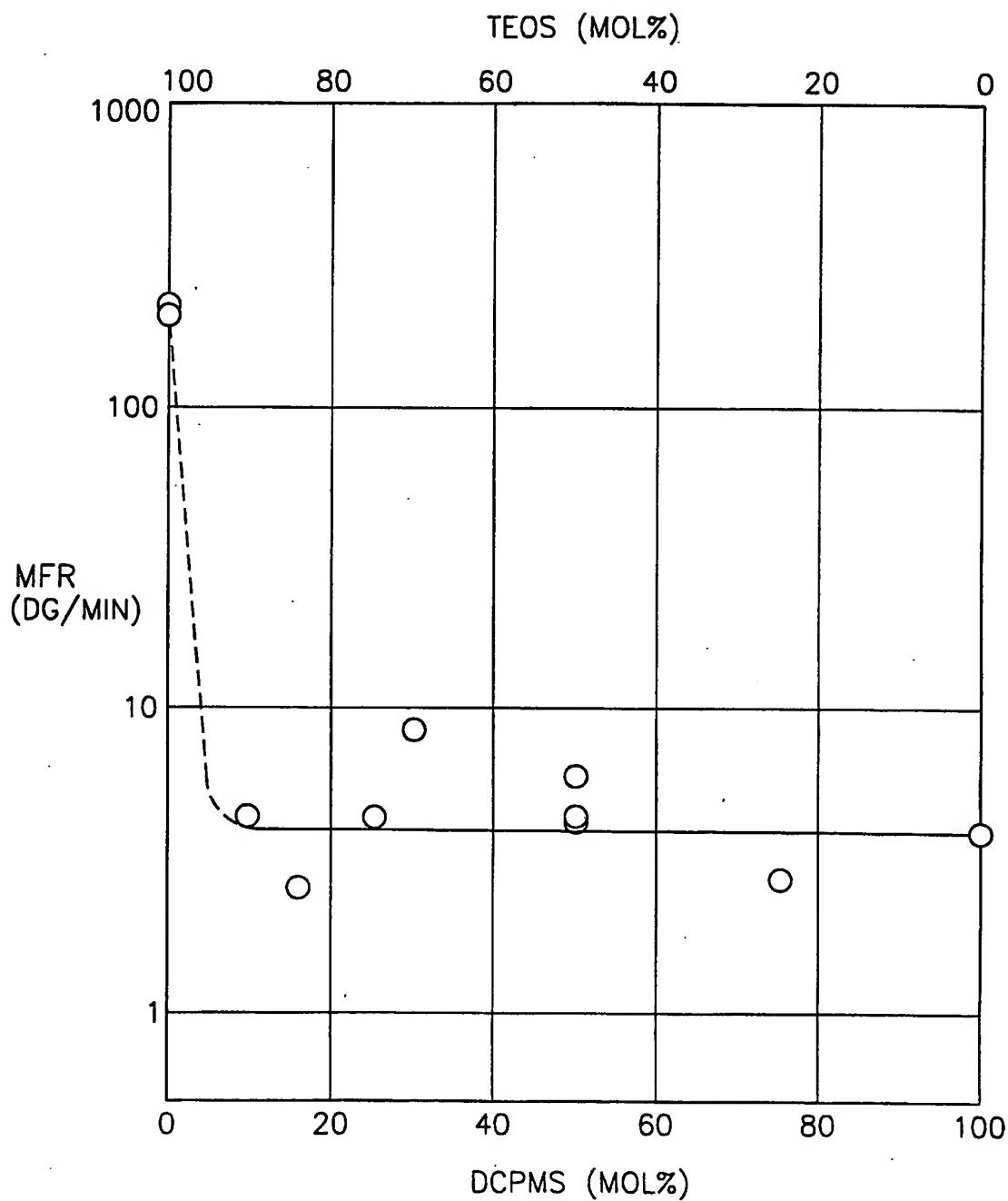


FIG.2

SUBSTITUTE SHEET (RULE 26)

3/4

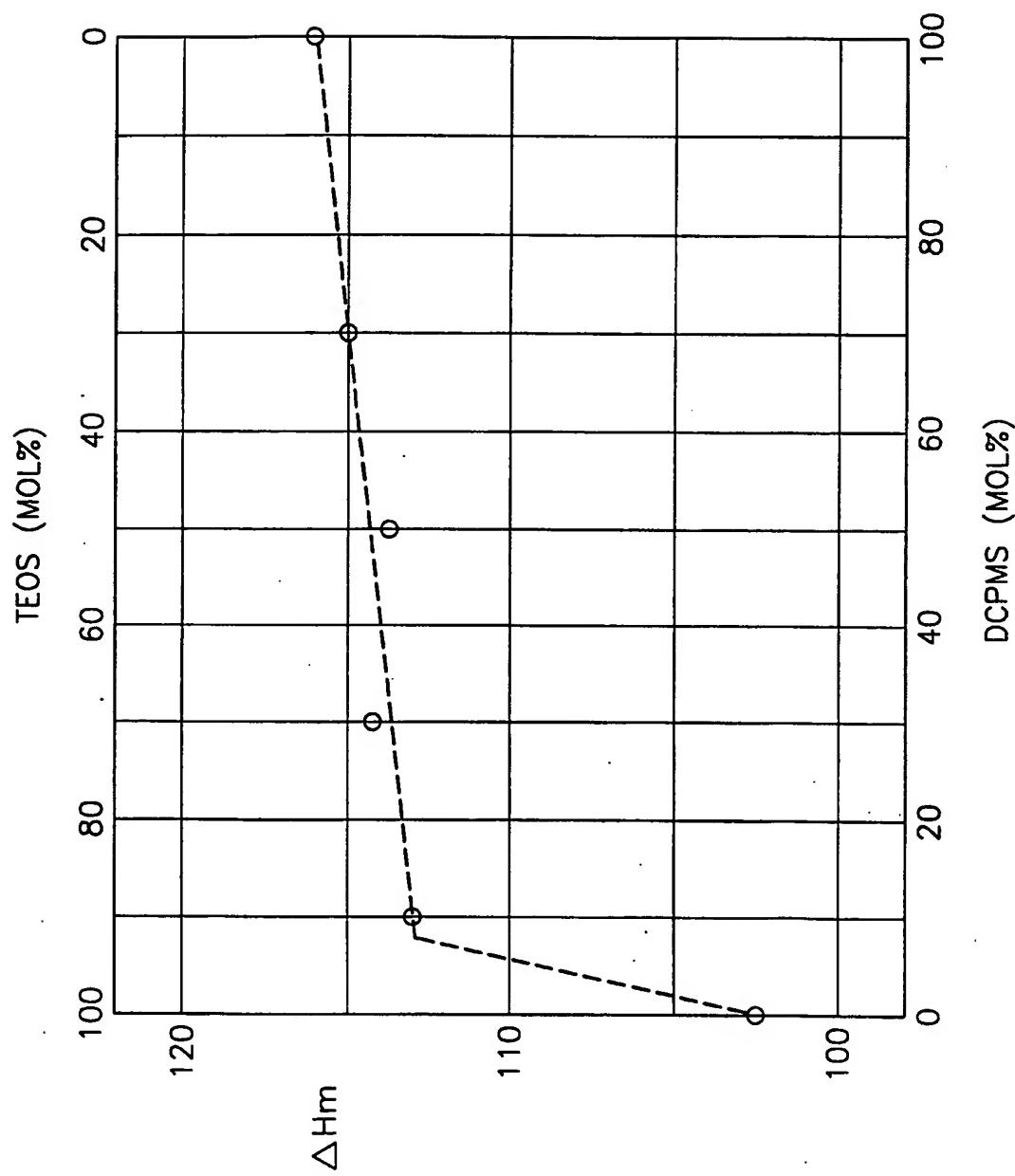
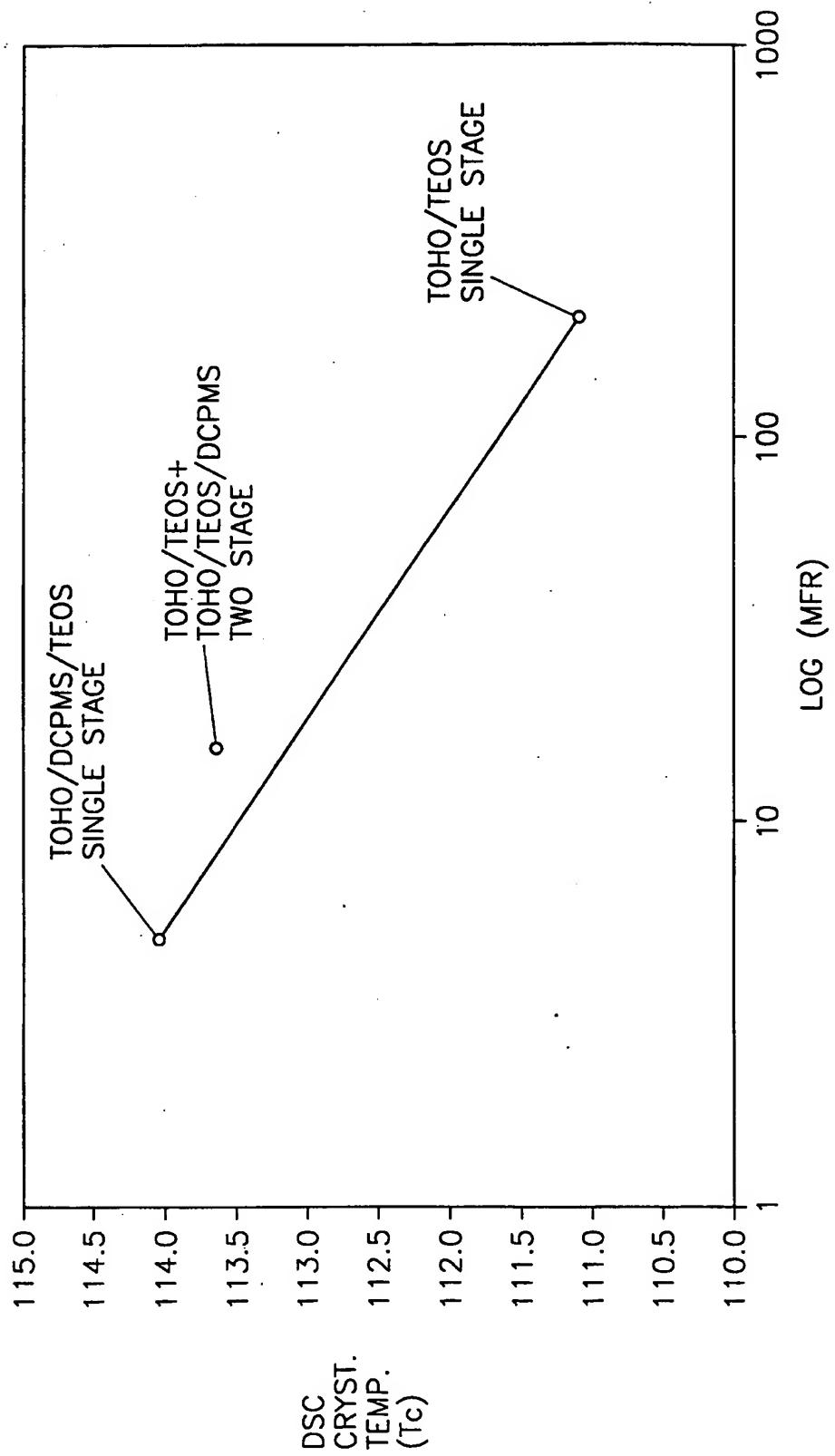


FIG. 3

4/4



SUBSTITUTE SHEET (RULE 26)

FIG. 4

INTERNATIONAL SEARCH REPORT

Internat'l Application No
PCT/US 95/01499A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 C08F10/00 C08F4/646

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 C08F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
P, X	EP,A,0 601 496 (MITSUI PETROCHEMICAL INDUSTRIES) 15 June 1994 see claims 2-5 see example 8 see comparative examples 1,4,5,8 see page 20; tables 1-2 see page 24; tables 2-1 ----	1-3,7,8
X	EP,A,0 385 765 (MITSUI PETROCHEMICAL INDUSTRIES) 5 September 1990 see examples 1-3 see page 13 - page 14; table 1 ----	1-3,7
A	EP,A,0 349 772 (HOECHST AKTIENGESELLSCHAFT) 10 January 1990 see claims 1,2 see the whole document -----	1

 Further documents are listed in the continuation of box C. Patent family members are listed in annex.

* Special categories of cited documents :

- *'A' document defining the general state of the art which is not considered to be of particular relevance
- *'E' earlier document but published on or after the international filing date
- *'L' document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- *'O' document referring to an oral disclosure, use, exhibition or other means
- *'P' document published prior to the international filing date but later than the priority date claimed

- *'T' later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- *'X' document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- *'Y' document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
- *'&' document member of the same patent family

Date of the actual completion of the international search 28 April 1995	Date of mailing of the international search report 06.06.95
Name and mailing address of the ISA European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax (+31-70) 340-3016	Authorized officer Fischer, B

INTERNATIONAL SEARCH REPORT

Information on patent family members

Intern. Application No

PCT/US 95/01499

Patent document cited in search report	Publication date	Patent family member(s)		Publication date
EP-A-0601496	15-06-94	CA-A-	2110606	05-06-94
		CN-A-	1090854	17-08-94
		JP-A-	6220121	09-08-94
		JP-A-	6220116	09-08-94
EP-A-0385765	05-09-90	CA-A-	2011188	02-09-90
		CN-A-	1045400	19-09-90
		JP-A-	3007703	14-01-91
EP-A-0349772	10-01-90	DE-A-	3819577	14-12-89
		AU-B-	621898	26-03-92
		AU-A-	3614889	14-12-89
		JP-A-	2070708	09-03-90
		US-A-	5100981	31-03-92

**This Page is Inserted by IFW Indexing and Scanning
Operations and is not part of the Official Record**

BEST AVAILABLE IMAGES

Defective images within this document are accurate representations of the original documents submitted by the applicant.

Defects in the images include but are not limited to the items checked:

- BLACK BORDERS**
- IMAGE CUT OFF AT TOP, BOTTOM OR SIDES**
- FADED TEXT OR DRAWING**
- BLURRED OR ILLEGIBLE TEXT OR DRAWING**
- SKEWED/SLANTED IMAGES**
- COLOR OR BLACK AND WHITE PHOTOGRAPHS**
- GRAY SCALE DOCUMENTS**
- LINES OR MARKS ON ORIGINAL DOCUMENT**
- REFERENCE(S) OR EXHIBIT(S) SUBMITTED ARE POOR QUALITY**
- OTHER:** _____

IMAGES ARE BEST AVAILABLE COPY.

As rescanning these documents will not correct the image problems checked, please do not report these problems to the IFW Image Problem Mailbox.